

IMPACT OF ENERGETICALLY ACCESSIBLE PROTON PERMUTATIONS IN THE SPECTROSCOPY AND DYNAMICS OF H_5^+

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H_5^+ has been proposed to be the intermediate of the astrochemically interesting proton transfer reaction $\text{H}_3^+ + \text{H}_2 \rightarrow \text{H}_2 + \text{H}_3^+$. The scrambling of five protons in this floppy, “structureless” ion introduces complications to its high-resolution rovibrational spectroscopy and the proton transfer dynamics between H_3^+ and H_2 . Quantum chemical studies are performed to predict and interpret the spectroscopic and dynamical properties of H_5^+ , with special consideration paid to the group theoretical aspects. If the full permutation of protons were allowed in H_5^+ , just like in CH_5^+ , the system should have been characterized by the G_{240} complete permutation-inversion group.^b However, our diffusion Monte Carlo calculations indicate that such a full permutation is not allowed for most of the molecular configurations sampled by the reaction path of the proton transfer process in question, and the energetically accessible permutations are functions of the distance between the H_3^+ and H_2 fragments.^c In the present study, we investigate two extreme geometries of H_5^+ , the $[\text{H}_2\text{-H-H}_2]^+$ shared-proton intermediate and the $\text{H}_3^+ \cdots \text{H}_2$ long-range complex, using two subgroups of G_{240} , G_{16} and G_{24} , respectively. In these two limiting circumstances, we derive the symmetry-adapted basis functions for the energy levels that describe the nuclear spins and the rovibrational motions of H_5^+ . Based on the results of these derivations, we discuss the spectroscopic properties of H_5^+ , including the coupling between different rovibrational degrees of freedom in the effective nuclear motion Hamiltonian, the electric-dipole selection rules for rovibrational spectroscopy, and correlations of energy levels between $[\text{H}_2\text{-H-H}_2]^+$ and $\text{H}_3^+ \cdots \text{H}_2$. Our study can be considered as the first step towards the implementation of future quantitative theoretical investigations for comparison with spectroscopic and dynamical experiments.^d

^aThe study was performed when Z. Lin was a graduate student with A. B. McCoy at The Ohio State University.

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